

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Bernard et al.

Serial No.: 09/630,517



Group Art Unit: 1714

Filed: August 02, 2000

Examiner: K. I. Wyrozebski Lee

For: POLYAMIDE NANOCOMPOSITES WITH OXYGEN SCAVENGING
CAPABILITYCommissioner of Patents and Trademarks
Washington, D.C. 20231#10/for
06.27.02DECLARATION UNDER 37 CFR 1.131

We, Linda G. Bernard, Horst Clauberg, Michael J. Cyr, John W. Gilmer, James C. Matayabas, Jr., Jeffery T. Owens, Mark E. Stewart, Sam R. Turner, and Shriram Bagrodia declare that:

1. We are the coinventors of claims 1-29 of the above-identified patent application.
2. Prior to August 5, 1999, having earlier conceived the idea of recyclable polymer nanocomposite with improved oxygen and gas barrier properties comprising at least one polyamide resin, at least one oxygen-scavenging catalyst, and at least one layered silicate material, Linda G. Bernard, Jeffrey T. Owens, Marvin C. Hagey, and John W. Gilmer prepared the following polyamide polymer compositions, described herein, at the Research Laboratories of Eastman Chemical Co., Kingsport, Tennessee.
 - A) The following general procedures were used to measure oxygen consumption and carbon dioxide permeability. Oxygen consumption was measured on film samples, which were cut into strips, using a Columbus Instruments Micro-Oxymax respirometer with version 6.04b software. Samples were placed into a glass media bottle with a nominal volume of 250 mL. One empty bottle was included as a control blank. The bottles were attached to a ten port expansion module. Readings were taken at the start of the experiment and

then every four hours. The instrument measured the change in the oxygen concentration from the previous reading in each cell and calculated the total oxygen consumption and rate based on the (previously measured) volume of the cell plus oxygen sensor system. The oxygen sensor is an electrochemical fuel cell. Carbon dioxide transmission rates were measured on film samples using a Mocon permeability analyzer.

- B) An unmodified MXD6 polyamide was prepared by extruding two trilayer films comprising internal layers of about 10 and 30 vol% of unmodified MXD6 6007, available from Mitsubishi Gas Company, with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were stretched using a T. M. Long instrument (4x4 orientation at about 110°C). The carbon dioxide transmission rates were 174 and 59 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively.

A MXD6 polyamide composition containing about 4000 ppm cobalt acetate as an oxygen-scavenging catalyst was prepared by mixing 250 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, and 4.23 grams of cobalt acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes then cooling. X-ray analysis of the product showed the concentration of cobalt in the product to be about 4000 ppm. This cobalt-containing polyamide (10 parts) was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company, at 250°C, to give material with a cobalt concentration about 400 ppm. The polyamide was used to prepare trilayer films and 2-inch square sections of the films were stretched as described above. The carbon dioxide transmission rates of the oriented films were determined to be 168 and 54 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner polyamide layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% polyamide, was determined to be about 370 microliters of oxygen over a period of 136 hours.

C) Using the procedure of example B, an MXD6 polyamide composition containing a layered silicate material and cobalt as an oxygen-scavenging catalyst was prepared by mixing 215.75 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, 34.25 grams of SCPX-1578, an organoclay available from Southern Clay Products, and 4.23 grams of cobalt(II) acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes followed by cooling. Ten parts of this product was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company at about 260°C to give material with a cobalt concentration of about 400 ppm and silicate concentration (ash) of about 1.0 wt%.

Two trilayer films were extruded comprising internal layers of about 10 and 30 vol% of the above compounded MXD6 6007 with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as described above. The carbon dioxide transmission rates for the oriented films were 117 and 41 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner nanocomposite layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% nanocomposite, was determined to be about 680 microliters of oxygen over a period of 136 hours.

D) Another MXD6 polyamide composition containing an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example B was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. A trilayer film was extruded comprising internal layers of about 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were prepared and oriented as above. The carbon dioxide transmissions rate of the oriented films were 411 cc(STP) CO₂/meter²/24hr, for the 50 vol% films. Oxygen consumption for 10

grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the PET-polyamide composite was determined to be about 60 microliters of oxygen over a period of 136 hours.

- E) Another MXD6 polyamide composition containing a layered silicate material and an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example C was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. Two trilayer films were extruded comprising internal layers of about 30 and 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as above. The carbon dioxide transmissions rates of the oriented films were determined to be 317 and 291 cc(STP) CO₂/meter²/24hr, for the 30 and 50 vol% films respectively. Oxygen consumption for 10 grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the nanocomposite was determined to be about 60 microliters of oxygen over a period of 136 hours.
- F) A polyamide composition was prepared in which the oxygen-scavenging catalyst, cobalt, was intercalated into the polymer matrix through the layered silicate material. A Wyoming-type montmorillonite clay was prepared in which 50% of the sodium cations were exchanged with cobalt and 50% with protons. Ash content of the clay was 87.15 wt %, cobalt content was 1.23 %, and X-ray basal spacing was 1.25 nm. The treated clay was dry mixed with 269 parts of a low molecular weight poly(m-xylylene adipamide), with IV of about 0.41 dL/g. The mixture was dried at 110°C overnight in a vacuum oven then extruded. The extruded material showed good oxygen consumption.
- G) Another polyamide composition was prepared identically to E except the montmorillonite clay used in the composition had 50 % of the sodium cations are exchanged with cobalt(II), 25% with octadecyltrimethylammonium cations,

and 25 % with protons. The clay had a cobalt content of 0.99 %, and X-ray basal spacing of 1.34 nm. The extruded material showed good oxygen consumption.

3. Evidence supporting the above examples above are provided by copies of research notebook pages as set forth in the table below and attached hereto:

Experiment	Supporting Notebook Pages	Performed by
B	X-26645-100 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
C	X-26645-101 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
D	X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
E	X-26645-101 X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
F	X-26640-085 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owens
G	X-26640-087 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owen

Further evidence of the conception of one aspect of this invention is provided by page X-25982-100 from Mr. Owens notebook, also attached hereto.

4. Each of the dates deleted from the attached notebook pages is prior to August 5, 1999.

The undersigned declares further that all statements made herein on his own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with a knowledge that willful, false statements, and the like so made are punishable by fine, or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

June 16, 2002
Date

Date

Date

June 4, 2002
Date

June 4, 2002
Date

June 4, 2002
Date

June 5, 2002
Date

June 7, 2002
Date

Linda Gail Bernard
Linda Gail Bernard

Horst Clauberg

Michael John Cyr

John Walker Gilmer
John Walker Gilmer

James Christopher Matayabas, Jr.

Jeffrey Todd Owens
Jeffrey Todd Owens

Mark Edward Stewart
Mark Edward Stewart

Sam Richard Turner
Sam Richard Turner

Docket: 71111

PATENT

June 10, 2002
Date

Shriram Bagrodia
Shriram Bagrodia

No 100

X 266

Preparation of D(ND) 4000 ppm Cobalt

Objective: Prepare the above to be let down into MXD6 @ 400 ppm Cobalt
 the final material will be used as the center layer in multilayer film
 and the goal is that the cobalt will act as an O₂ scavenger.

Preparation: The following were weighed into a $\frac{3}{4}$ /₄₅ single-neck, 1L, round-bottom flask and heated until melted while stirring slowly under strong N₂ purge. When the material is removed from the N₂ saturated flask, it will be enclosed in a plastic bag to break up into pieces, placed in a glass (quart Kerr Jar) container and then placed in an oven @ 80°C under nitrogen.

R&N#	Grams Needed	Comments
D(ND)	250	Batch 961002b1
Cobalt Acetate	4.23	Lot 4519 KEVP Mallinckrodt

Report: Reactor C Date: [REDACTED] Time: 15:17:51

Recipe Name: C:\CAMILETG\RECIPES\ND_CO.RCP

Notebook Name: X26645-100

Flags: S=Stirrer Slaved, T=Service Traps, C=Add Catalyst

Stage	Time	Temp	Vac	Stir	Power	Flags	Estimated End Time
	Min	°C	Torr	RPM	%	S T C	
1	1	245	730	0	0	0 0 0	15:18:51
2	120	245*	730	250	0	0 0 0	17:18:51

*I had to increase this temp. to 250°C to get the D(ND) to melt so the Cobalt could be stirred into the polyamide.

Note: When I got ready to remove the polyamide from the polymer rig, I kept the flask under N₂ flow as long as I could, then I broke the flask quickly, broke the polyamide as best as I could using a cloth, plastic bag & a hammer. The chunks were not small enough; therefore, I placed the chunks in a quart Kerr jar & put it in the oven @ 80°C & a good N₂ flow. Later I removed the jar from the oven, sealed it & broke the chunks further with the polymer chopper. I will grind them tomorrow. Igf [REDACTED]

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

DATE [REDACTED]

DATE [REDACTED]

X 26645

No 101

Preparation of D(ND) / ^{1st} 10.0 wt% SCPX-1578 / 4000 PPM Cobalt

Objective and Procedure: See P-100

RxNt	Grams Needed	Comments
D(ND)	215.75	Batch 96100261
SCPX-1578	34.25	Southern Clay Products
Cobalt Acetate	4.23	Lot 4519 K EVP Mallinckrodt

Report: Reactor D Date: _____ Time: 15:18:24

Recipe Name: C:\CAMILETG\RECIPES\ND_C0.RCP

Notebook Name: X26645-101

Flags: S=Stirrer Slaved, T=Service Traps, C>Add Catalyst

Stage	Time Min	Temp °C	Vac Torr	Stir RPM	Power	Flags				Estimated End Time
						S	T	C		
1	1	245	730	0		0	0	0	0	15:19:24
2	120	245*	730	250		0	0	0	0	17:19:24

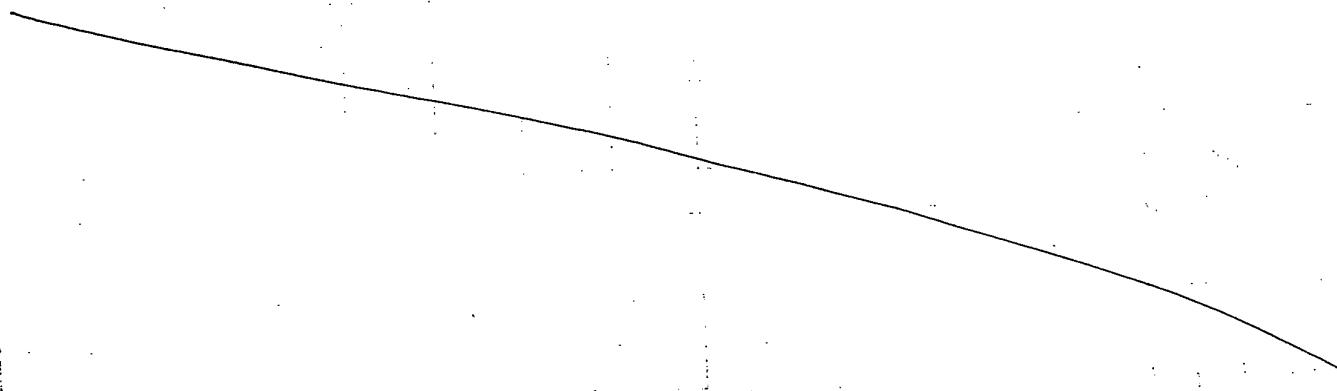
* I had to increase the temp of this run to 260°C to get the polyamide to melt and distribute the Cobalt + clay throughout the polyamide.

See note on P-100 for removal and chopping method. 1st [REDACTED]

Analysis of 100 and 101: X-Ray wt% Ash = 10.32%

$$100 = 4,000 \text{ PPM Cobalt or } 0.40\%$$

$$101 = 3,800 \text{ " " or } 0.38\%$$



TEC 6573-3

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

Linda Bernard
Hiltsie Malina

DATE

DATE

X 26645

No 103

168 [REDACTED]
SCPX-1578

Submitted MXD6/D(ND)/EWC-ODA/Cobalt Samples For Compounding
Objective: Compound the above @ 400 ppm Cobalt and 10 wt%
Silicate to be used in tri-layer film extrusion to act as an
oxygen scavenger.

Procedure: Mixed the following in 2-1/2 gallon jars.

Item	MXD6	D(ND)/Cobalt	D(ND)/EWC-ODA/Cobalt
1	1080g	120 g	Reference = X26645-101
		Reference = X26645-100	SCPX-1578 168 [REDACTED]
2	1080g	120g	Reference = X26645-101
	Reference = Grade 6007		
	Lot # S80106		

Linda Bernard [REDACTED]

Item	MXD6 Ref: Grade 6007 Lot # S10806	D(ND)/Cobalt Ref: X26645-100	D(ND)/EWC-ODA/Cobalt Ref: X26645-101	Total Grams
1	1080	120		1200
2	1080		120	1200

PAGE

BOOK

No 106

X 25036

Linda Bernard EXT. 8060 R.12560
X-26645-103 - 1,2

ZONE TEMP. SET PT. 1. 2. 3. 4. 5. 6. 7. 8.
240 260 260 260 260 260 260 260
103-1 ACTUAL 240 260 260 261 260 260 260 260
103-2 ACTUAL 240 260 260 260 260 260 260 260

	MELTPESS.	MELTTEMP.	TORQUE	FEEDER ST.	RPM	
103-1	170	253	72	7	250	
103-2	190	254	73	5	250	
						SCPX-1578 168 [REDACTED]
	MXD6 Ref: Grade 6007 Lot # S10806	D(ND)/Cobalt Ref: X26645-100	D(ND)/EWC-ODA/Cobalt Ref: X26645-101			Total Grams
1	1080	120				1200
2	1080		120			1200

SIGNATURE OF AUTHOR Bill Parker DATE [REDACTED]

SIGNATURE OF WITNESS _____ DATE _____

TEC 6573-4 (2-82)

TEC 6573-3

SIGNATURE OF AUTHOR Linda Bernard DATE [REDACTED]

SIGNATURE OF WITNESS Patricia Williams DATE [REDACTED]

X-Ray Analysis:
Item #1 = 476 ppm Cobalt
Item #2 = 441 ppm Cobalt
Retested by ICP [REDACTED]

Ash Analysis:
Item #1 = 0.04 w/w
" #2 = 1.06 w/w

Retested by ICP
for ppm Co:

Item #1 = 3.96 ppm Co
" #2 = 3.20 ppm Co

X 26645

No 113

Submitted Cobalt Materials to be Compounded w/ PET 20261
16 ppm [REDACTED]

Objective & Procedure: See P-003

Submitted on [REDACTED] 2018

Linda Bernard

X-Ray Analysis:

Item #1 = 16 ppm Co.
" #2 = 16 " "

page

Nº 108

BOOK

Linda Bernard
X 26645 - 113-1-2

Ash Analysis:

Item #1 = 0 wt%
1

11 #2 = 0.0516 wt% Ash

Temp Set	1	2	3	4	5	6	7	8
113 - 1	100	275	275	275	275	275	275	275
Actual	100	279	275	275	275	275	275	262

	Melt Press	Melt Temp.	Torque	Feedin Set	RPM
113-1	190	246	85	3	315
113-2	200	241	75	3	315

X26645-113-					
Item	Reference of PET	Material Added	Reference of Co Additive	Grams of PET	Grams of Co Additive
1	Amber - 20261	MXD6(D(ND)Cobalt	X26645-103-1	1920	80
2	Amber - 20261	MXD6(D(ND)SCPX-1578/Cobalt	X26645-103-2	1920	80
					2000

SIGNATURE OF AUTHOR *R. McConnel*

... DATE

۱۰۵

SIGNATURE OF WITNESS

10

TEC 6573-3 (2-88)

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESSES

Lynda Bernard

Schroeder William

DA

88

X 26645

No 117

Submitted Samples to David Jesse To Be Used in Tri Layer Film Extrusion

Objective: Determine How Effective the Materials are in enhancing Barrier Properties and Adhesion of the Layers Containing AQ48.

Procedure: Submitted the Samples VIA B-125's electronic Submission Form. Delivered the MXD6 10wt% AQ48 and MXD6 20 wt% AQ48 to David Jesse for him to dry, but kept the other (Cobalt) Samples under N₂ flow Atmosphere.

The Following Materials were Submitted:

Item #	Reference for Center Layer	Center Layer Composition	Center Layer (Grams Submitted)	Outer Layer (Provided by B-125)
1	X26645-103-1	MXD6/D(ND)/Cobalt	500	9921
2	X26645-103-2	MXD6/D(ND)/SCPX-1578/Cobalt	500	9921
3	X26645-113-1	Amber PET 20261 4.0 wt% MXD6/D(ND)/Cobalt	1000	9921
4	X26645-113-2	Amber PET 20261 4.0 wt% MXD6/D(ND)/SCPX-1578/Cobalt	1000	9921
5	X26645-072-1	MXD6 10.0 wt% AQ48	1000	9921
6	X26645-072-2	MXD6 20.0 wt% AQ48	1000	9921

PPARL Processing Requests
B125 DOOR E0

All requests must have a charge number

Submitter Linda Bernard Ext. 8060 Bldg. 150A Date [REDACTED]
Project Name Beer Charge No. R.12562
Polymer Type A Mixture of MXD6/D(ND)/COBALT/CLAY/PET 20216

Processing Machine
David, if I did not indicate the correct machine, please use the machine you used when processing our previous samples. Linda
 Small Killion (Thin Film) Injection Molding (Preform)
 Screw General Purpose Mold _____
 Large Killion (Thin Film) Reheat Blow (Bottles)
 Screw Free-blow (Bottles)
 MPM (Thick Film or Sheet) Pipe Extrusion
 Screw Crystallizer
 Blown Film Other _____

Polymer Drying Conditions: Temperature 120°C Time 24 Hours
Flush Material 9921 for the extruder feeding the A Layers; MXD6 and PET 20261 for the extruder feeding Layer B.
Processing Temp: Melt 265°C Roll _____ Mold _____
Film No. Layers 3 Thickness *(See Note) Width _____ Polished _____
Disposition of Excess Resin Same as PET Film

*MXD6/Cobalt and the MXD6/AQ48 Materials-We want Layer B to be 10 and 30% of the total thickness. The PET/MXD6/Cobalt materials-We want Layer B to be 10 and 50% of the total thickness.

Sample Description

Reference No. Instructions	Quantity	Comments / Special
X26645-117-1	500 to 600 grams	MXD6/D(ND)/COBALT
X26645-117-2	500 to 600 grams	MXD6/D(ND)/SCPX-1578/COBALT
X26645-117-3	1000 grams	AMBER PET 20261/MXD6/D(ND)/COBALT
X26645-117-4	1000 grams	AMBER PET 20261/MXD6/D(ND)/CLAY/COBALT
X26645-117-5	1000 grams	MXD6/AQ48
X26645-117-6	1000 grams	MXD6/AQ48

Submit request to David M.Jesse B125 (X-7373) U835201 FAX 6183

Processing Lab: Steve Darnell, Danny Glover, Mike Jones (X-5663)

David, I may be sending more of X26645-117-1 and 2 than what I listed, I am not sure how much I have. We want the B layer to be 10 and 30% of the total for -117-1, -117-2, -117-5 and -117-6, we want the B-layer to be 30 and 50% of the total thickness of -117-3 and -117-4. I wrote all this on the processing form, but just thought I would reiterate it. Thank you for taking care of this for us. I will carry the MXD6/AQ48 samples out there because I need to check with Danny Glover about a sample that we never received. Linda.

TEC 6573-3

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

Linda Bernard
Matthew J. Williams

DATE

DATE

X 26645

No 123

Received Films (TriLayer) That were Submitted on P-117 And
 Submitted them For ~~TM Long Stretch~~, Etc.
 Optical Measurements, 180 Peel

Objective: Have the film stretched and the PO_2
 Tested to determine if the Cobalt and/or
 SCPX-1578 improves on O_2 Barrier. The
 AG Samples are to be tested for improvement on adhesion.

Procedure: The 8 Samples containing Cobalt were cut and placed in a bag that was then filled w/ N_2 and Kept this way until stretched. After stretching I am requesting that they be put back under N_2 until they are placed on the Oxotran 220 cells to be tested for PO_2 .

Linda Bernard [REDACTED]

Note: TM-Long Stretch and related data on P-124. lgb.

TEC 6573-3

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

Linda Bernard
 Linda Willim

DATE [REDACTED]

DATE [REDACTED]

X26645-123:		Reference of Center Layer	Composition of Center Layer	Center Layer (Tangal Vol%)	Outer Layers of TriLayer Films	B-125 Reference low (gmm/mm)	180 Peel high (gmm/mm)	181 Peel low (gmm/mm)	Top Layer	Center Layer	Bottom Layer	Barrier (% Vol)
1		Lot 6007	MD6	10	9921 X26736-052-A	0.8/2	2.9/3	2.9/3	160	47	220	10
2		Lot 6007	MD6	30	9921 X26736-052-B	--	3.7/5	130	170	190	35	
3		Lot 6007	MD6	50	9921 X26736-052-C	--	88	270	120	56	-	
4		X26645-117-5	MD6 10 w/w% AQ48	10	9921 X26736-054-5	1.0/5	--	160	63	210	13	
5		X26645-117-5	MD6 10 w/w% AQ48	30	9921 X26736-054-5	4.3/4	9.7/1	100	140	220	30	
6		X26645-117-6	MD6 20 w/w% AQ48	10	9921 X26736-054-6	0.8/5	--	130	63	280	13	
7		X26645-117-6	MD6 20 w/w% AQ48	30	9921 X26736-054-6	6.2/3	13.5/2	130	210	190	40	
8		X26645-117-1	MD6(DND)/Cobalt	10	9921 X26736-054-1	--	--	150	39	250	9	
9		X26645-117-1	MD6(DND)/Cobalt	30	9921 X26736-054-1	--	--	130	150	210	31	
10		X26645-117-2	MD6(DND)/SCPX-1578/Cobalt	10	9921 X26736-054-2	--	--	150	50	280	11	
11		X26645-117-2	MD6(DND)/SCPX-1578/Cobalt	30	9921 X26736-054-2	--	--	110	180	180	38	
12		X26645-117-3	Amber PET 2026/IMXD6(DND)/Cobalt	30	9921 X26736-054-3	--	--	99	130	200	30	
13		X26645-117-3	Amber PET 2026/IMXD6(DND)/Cobalt	50	9921 X26736-054-3	--	--	84	170	120	45	
14		X26645-117-4	Amber PET 2026/IMXD6(DND)/SCPX-1578/Cobalt	30	9921 X26736-054-4	--	--	130	140	190	30	
15		X26645-117-4	Amber PET 2026/IMXD6(DND)/SCPX-1578/Cobalt	50	9921 X26736-054-4	--	--	86	210	120	50	

No 124

X 26645

PEL Submission For Tri-Layer Film on P-123 For TM-Long Stretch, 180 Peel,
Color & Haze

Polymers Evaluation Laboratory	
PEL Submission Form	
Submitter: LINDA BERNARD Date: _____	
Insurance #: 792460	Chargew. O. #: RJ2560
Building #: 150	VAX User ID: UP92460
Phone #: 8060	Presigned PEL #: _____

- Project Category: 4 • Target Date: _____
- Application: 4 • Project #: _____
- Overtime is authorized to meet this target date: no

Click on "Notebook #" item to enter the next material

X26645-123-1	X26645-123-9
X26645-123-2	X26645-123-10
X26645-123-3	X26645-123-11
X26645-123-4	X26645-123-12
X26645-123-5	X26645-123-13
X26645-123-6	X26645-123-14
X26645-123-7	X26645-123-15
X26645-123-8	Notebook #

• Hazards: no
 Submitter Pretreatments Enter results into PDRS: no
 • Testing ... Return Excess Sample: yes

Film Checklist	Notebook Number	123-1	123-2	123-3	123-4	123-5	123-6	123-7	123-8	123-9	123-10	123-11	123-12	123-13	123-14	123-15
Acetalsolve	Test Cond.															
Ash	Test Cond.															
Capillary Rheometer	Test Cond.															
Coef. of Friction	Test Cond.															
Density	Test Cond.															
Elongation at Break	Test Cond.															
Melt Flow Rate	Test Cond.															
CO ₂ Permeability	Test Cond.															
Instrumented Impact	Test Cond.															
IV	Test Cond.															
O ₂ Permeability	Test Cond.															
Reference Index	Test Cond.															
Film Tensile Force (1013Pa)	Test Cond.															
Film Heat Distortion Temperature (HDT)	Test Cond.															
Film Tensile Properties (TENS2)	Test Cond.															
Thermal Analysis	Test Cond.															
T-NI Long Film Stretch	Test Cond.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Transparency	Test Cond.															
Water Vapor Permeability	Test Cond.															
180 Peel	Test Cond.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

Polymers Evaluation Laboratory	
T. M. Long Film Stretching Test Request	
• Stretch Temp (Deg. C): 105	
• Stretch Temp (Deg. C):	
• Stretch Temp (Deg. C):	
• Stretch Ratios: 4X4	
• Stretch Ratios:	
• Tg (Deg. C): -83	
• Stress Strain: yes	
• Machine: 4X	
• Number of Sheets: 3	
• Stretch Rate: 14 in/sec	
• PSR (4X by 4X only and 14 in/sec): yes	
Previous Stretch conditions (if known)	
• Grip Pressure:	
• Soak Time: 60 SEC	
• Previous Stretch Temp (Deg. C):	
Comments RANDY, SAMPLES # 8 THROUGH 15 NEED TO BE KEPT UNDER NITROGEN AS MUCH AS POSSIBLE. I AM SENDING THEM TO YOU IN A BAG THAT HAS BEEN FILLED WITH N2. IF YOU WOULD PUT THEM IN A BAG AND FILL IT WITH N2 AFTER STRETCHING I SURE WOULD APPRECIATE IT. THANK YOU LINDA	

X26645-124:	Item Reference	Oxygen Permeability (cc milliliter ⁻² 24-H atm) (cc CO ₂ milliliter ⁻² 24-H atm)	Carbon Dioxide (Permeability) (Transmission Rate) (cc CO ₂ milliliter ⁻² 24-H atm) (cc CO ₂ milliliter ⁻² 24-H)	Carbon Dioxide (Transmission Rate) Hazb (%)	L*	a*	b*	180 Peel low#	180 Peel high#	Top Layer (μm)	Center Layer (μm)	Bottom Layer (μm)	Barrier Layer (% Vol)	PSR (A/g)		
1 X26645-123-1	2.70	16.62	174.32	0.58	94.48	-0.77	-0.20	0.243	0.5/2	13.0	4.0	21.0	11	15.08		
2 X26645-123-2	0.8	5.86	58.58	1.68	94.91	-0.87	-0.16	0.1/3	0.8/2	14.0	14.0	26.0	2.6	13.4		
3 X26645-123-3	4.79	#VALUE!	..	
4 X26645-123-4	5.52	
5 X26645-123-5	1.12	
6 X26645-123-6	3.41	
7 X26645-123-7	
8 X26645-123-8	2.47/2.11	14.66	168.17	0.31	94.37	-0.91	-0.19	did not peel	did not peel	11.3	5.6	24.0	1.4	15.01		
9 X26645-123-9	0.81/0.68	4.54	53.73	0.71	94.88	-0.91	-0.04	44.64	94.66	0.92	0.05	12.5	16.5	25.5	3.0	14.41
10 X26645-123-10	1.93/1.84	10.88	117.47	0.79	94.98	-0.89	-0.15	6.54	94.69	-0.89	0.10	12.3	4.9	21.7	1.3	15.08
11 X26645-123-11	0.69/0.51	3.91	40.76	2.33	94.73	-0.90	0.10	did not peel	did not peel	11.0	12.5	18.5	3.0	12.73		
12 X26645-123-12	6.63/6.05	3.20	33.75	0.43	92.67	-3.60	10.41	11.0	9.5	22.0	2.2	13.13		
13 X26645-123-13	6.5/16.13	25.17	410.73	0.43	92.06	-4.01	12.50	8.2	13.0	11.0	40	14.56		
14 X26645-123-14	6.5/36.20	27.45	317.38	0.43	92.01	-3.98	12.46	9.0	11.0	15.0	3.1	13.43		
15 X26645-123-15	5.9/25.66	22.98	280.93	0.39	91.13	-4.44	15.55	8.3	13.7	7.2	4.7	14.27		

SIGNATURE OF AUTHOR

Linda Bernard

DATE

TEC 65734

SIGNATURE OF WITNESS

Dentide Williams

DATE

X 26854

No 1 015

Sample	Kilay	Gel. Day	g/m²
sample 1	x 26840 - 87	13. 4	270
sample 2	x 26840 - 85	13. 2	269
sample 3	x 26840 - 86	6. 6	264

Extrusion on M-18 @ 275 rpm.

temp profile

zone 2	-	230°C	die pressure	20
zone 3		240°C	melt T	236°C
zone 4		240°C		
zone 5		240°C		
zone 6		245°C		
zone 7		245°C		
zone 8		250°C		
die		250°C		

TEC 6876

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

DATE

DATE

X 26640

No 085

X - 26640 - 85

This work is to prepare more of X26640-80

Suspend 2.36 g of cobalt(II)acetate tetrahydrate in 200 ml of water.

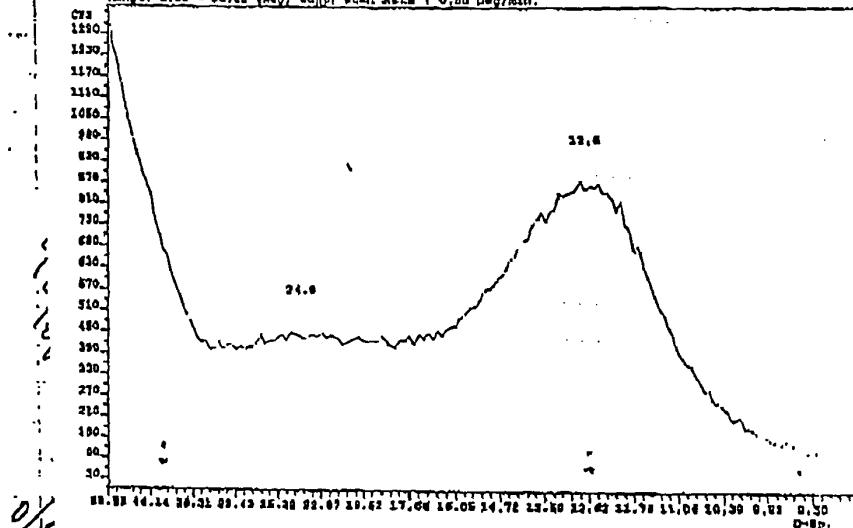
Suspend 40.0 g of SCPX-1276 in 2000 ml of hot water at 80 °C in a Commercial Waring Blender and blend for two minutes.

Add the Cobalt solution to the Waring Blender and blend for two minutes.

Add $\frac{50}{50}$ ml of 0.962 N HCl and blend for two minutes.

Centrifuge the mixture and pour off the water. Wash with 1000 ml of water in blender.

Y4301 X26640-85, XRD X26640-85
Date: 04/18/89 34:02 Step: 0.004° Cnt: 10000 Max.
Range: 2.00 - 10.00 (deg) Comp: Scan Rate: 0.00 deg/min.



TEO 8673-3

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

DATE

DATE



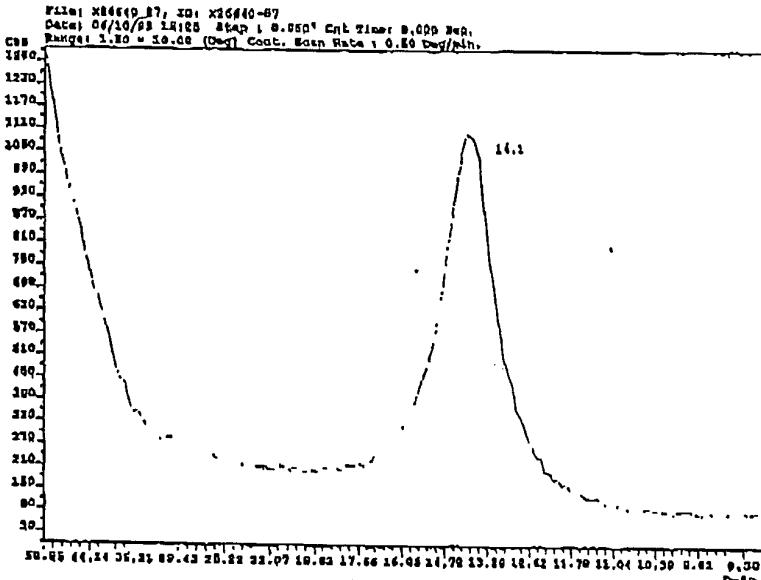
X 26640

No 087

THIS WORK IS TO PREPARE
AN ORGANOCOBYL CONTAINING CO
AND OCTADECYL TRI METHYLAMMONIUM
WITH A SODIUM THAT WILL
BE DISPLACED WITH IT.

THIS CLAY SHOULD CONTAIN 47.5
MGS OF COBYL 23.75 MGS OF
OCTADECYL TRI METHYLAMMONIUM
AND 23.75 MGS AMINOPOLYAMIDE.

SUSPEND 2.36 G (MW 249.08)
OF COBALT II ACETATE TETRAHYDRATE
AND 6.56 G OF ARGOUD 18-SO
IN 200ML OF WATER.



12.76 1.16
A-T 80°C
ANP
NOTES.

1.0F
END FOR.

84.88%
REMOVED
A
REMOVED
END
WAS DRIED
OVER

AT 60°C OVER NIGHT. COBALT = 1.14%
YIELD = 28.6 MS. SPION = 7.5%

No

122



X 25982

Properties of Montmorillonite with Cobalt and H+

Table 1. MXD6 with Montmorillonite Clay Containing Co⁺⁺ and H⁺

X26854-15-	Composition	1 Montmorillonite 50% Co ⁺⁺ 25% H ⁺ 25% octadecyl trimethyl ammonium	2 Montmorillonite 50% Co ⁺⁺ 50% H ⁺⁺	3 Montmorillonite 100% H ⁺
Ash	%	4.44	3.84	1.75
DSC (pellet)	°C	203	88/199	209
Tch1	°C	237	237	239
Tm1	°C	81	82	82
Tg	°C	133/198	134/198	139/200
Tch2	°C	236	236	236
Tm2	°C	181	181	178
Tcc		none observed	none observed	none observed
WAXD Basal Spacing			1.4	1.38
WAXD Intensity			8633	2755
TEM Images		Tactoids	Tactoids	Tactoids

SIGNATURE OF AUTHOR

Jeffrey T. Durvene

DATE

TEC 6573-4

SIGNATURE OF WITNESS

Charles M. Deary

DATE

No 100



X 25982

(CONT. from page 99)

Discussion of LCP and Clays / MXD6-Cobalt Ideas

Owens, Jeff

From: [REDACTED] Gilmer, John W
To: [REDACTED]
Subject: Owens, Jeff
FW: OAT form

----Original Message----

From: Dawsey, Timothy R
[REDACTED]
To: Gilmer, John W
Subject: FW: OAT form

----Original Message----

From: FrontPage.Email.Form@eastman.com [SMTP:FrontPage.Email.Form@eastman.com]
To: [REDACTED]
u836177%ntmcon02.emn.com.u856790%ntmcon02.emn.com.u790667%ntmcon02.emn.com.u858447%
ntmcon02.emn.com.u791425%ntmcon02.emn.com.u791320@eastman.com ; ; ; ; ;
Subject: OAT form

BO Requested: NBG, CPBO, SPBO
Username: Jeff Owens
UserTel: 7328
Contact: [REDACTED]

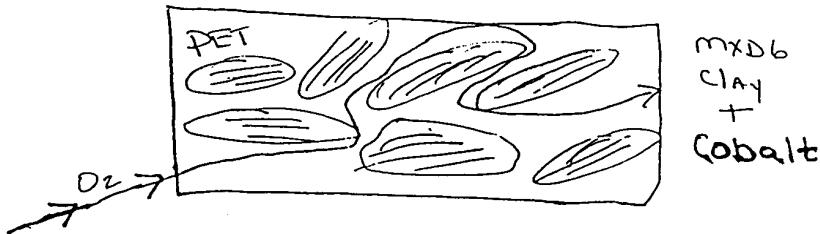
Time: 11:02:11 AM
Remote User: EASTMAN\U857191

Comments:

I recently read an article showing Oxygen permeability vs. Water vapor data for several resins these included PET, Nylon and LCP. LCP was by far the most superior with respect to permeability. I am sure there is data on PET/LCP blends but I thought the idea of put clay in LCP and making a trilayer film in PET would be interesting since we produce LCP we could buy it at our cost which might be cheaper than buying MXD6 Nylon.

Idea on Combining MXD6 Nylon with clay and Cobalt

I discussed with Dr. Chris Matayabas the idea of using the combination high barrier MXD6 nanocomposite with oxygen scavenging of Cobalt in the polymer matrix. In theory the O₂ molecules that flowed thru the nanocomposite would be cleaved by the Cobalt thus providing a material with better barrier potential in the market place with respect the beer.



(CONT. TO PAGE 123)

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

DATE

DATE

TEC 6573-4

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Bernard et al.

Serial No.: 09/630,517

Group Art Unit: 1714

Filed: August 02, 2000

Examiner: K. I. Wyrozebski Lee

For: POLYAMIDE NANOCOMPOSITES WITH OXYGEN SCAVENGING
CAPABILITYCommissioner of Patents and Trademarks
Washington, D.C. 20231**DECLARATION UNDER 37 CFR 1.131**

We, Linda G. Bernard, Horst Clauberg, Michael J. Cyr, John W. Gilmer, James C. Matayabas, Jr., Jeffery T. Owens, Mark E. Stewart, Sam R. Turner, and Shriram Bagrodia declare that:

1. We are the coinventors of claims 1-29 of the above-identified patent application.
2. Prior to August 5, 1999, having earlier conceived the idea of recyclable polymer nanocomposite with improved oxygen and gas barrier properties comprising at least one polyamide resin, at least one oxygen-scavenging catalyst, and at least one layered silicate material, Linda G. Bernard, Jeffrey T. Owens, Marvin C. Hagey, and John W. Gilmer prepared the following polyamide polymer compositions, described herein, at the Research Laboratories of Eastman Chemical Co., Kingsport, Tennessee.
 - A) The following general procedures were used to measure oxygen consumption and carbon dioxide permeability. Oxygen consumption was measured on film samples, which were cut into strips, using a Columbus Instruments Micro-Oxymax respirometer with version 6.04b software. Samples were placed into a glass media bottle with a nominal volume of 250 mL. One empty bottle was included as a control blank. The bottles were attached to a ten port expansion module. Readings were taken at the start of the experiment and

then every four hours. The instrument measured the change in the oxygen concentration from the previous reading in each cell and calculated the total oxygen consumption and rate based on the (previously measured) volume of the cell plus oxygen sensor system. The oxygen sensor is an electrochemical fuel cell. Carbon dioxide transmission rates were measured on film samples using a Mocon permeability analyzer.

- B) An unmodified MXD6 polyamide was prepared by extruding two trilayer films comprising internal layers of about 10 and 30 vol% of unmodified MXD6 6007, available from Mitsubishi Gas Company, with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were stretched using a T. M. Long instrument (4x4 orientation at about 110°C). The carbon dioxide transmission rates were 174 and 59 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively.

A MXD6 polyamide composition containing about 4000 ppm cobalt acetate as an oxygen-scavenging catalyst was prepared by mixing 250 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, and 4.23 grams of cobalt acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes then cooling. X-ray analysis of the product showed the concentration of cobalt in the product to be about 4000 ppm. This cobalt-containing polyamide (10 parts) was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company, at 250°C, to give material with a cobalt concentration about 400 ppm. The polyamide was used to prepare trilayer films and 2-inch square sections of the films were stretched as described above. The carbon dioxide transmission rates of the oriented films were determined to be 168 and 54 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner polyamide layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% polyamide, was determined to be about 370 microliters of oxygen over a period of 136 hours.

C) Using the procedure of example B, an MXD6 polyamide composition containing a layered silicate material and cobalt as an oxygen-scavenging catalyst was prepared by mixing 215.75 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, 34.25 grams of SCPX-1578, an organoclay available from Southern Clay Products, and 4.23 grams of cobalt(II) acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes followed by cooling. Ten parts of this product was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company at about 260°C to give material with a cobalt concentration of about 400 ppm and silicate concentration (ash) of about 1.0 wt%.

Two trilayer films were extruded comprising internal layers of about 10 and 30 vol% of the above compounded MXD6 6007 with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as described above. The carbon dioxide transmission rates for the oriented films were 117 and 41 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner nanocomposite layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% nanocomposite, was determined to be about 680 microliters of oxygen over a period of 136 hours.

D) Another MXD6 polyamide composition containing an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example B was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. A trilayer film was extruded comprising internal layers of about 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were prepared and oriented as above. The carbon dioxide transmissions rate of the oriented films were 411 cc(STP) CO₂/meter²/24hr, for the 50 vol% films. Oxygen consumption for 10

grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the PET-polyamide composite was determined to be about 60 microliters of oxygen over a period of 136 hours.

- E) Another MXD6 polyamide composition containing a layered silicate material and an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example C was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. Two trilayer films were extruded comprising internal layers of about 30 and 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as above. The carbon dioxide transmissions rates of the oriented films were determined to be 317 and 291 cc(STP) CO₂/meter²/24hr, for the 30 and 50 vol% films respectively. Oxygen consumption for 10 grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the nanocomposite was determined to be about 60 microliters of oxygen over a period of 136 hours.
- F) A polyamide composition was prepared in which the oxygen-scavenging catalyst, cobalt, was intercalated into the polymer matrix through the layered silicate material. A Wyoming-type montmorillonite clay was prepared in which 50% of the sodium cations were exchanged with cobalt and 50% with protons. Ash content of the clay was 87.15 wt %, cobalt content was 1.23 %, and X-ray basal spacing was 1.25 nm. The treated clay was dry mixed with 269 parts of a low molecular weight poly(m-xylylene adipamide), with IV of about 0.41 dL/g. The mixture was dried at 110°C overnight in a vacuum oven then extruded. The extruded material showed good oxygen consumption.
- G) Another polyamide composition was prepared identically to E except the montmorillonite clay used in the composition had 50 % of the sodium cations are exchanged with cobalt(II), 25% with octadecyltrimethylammonium cations,

and 25 % with protons. The clay had a cobalt content of 0.99 %, and X-ray basal spacing of 1.34 nm. The extruded material showed good oxygen consumption.

3. Evidence supporting the above examples above are provided by copies of research notebook pages as set forth in the table below and attached hereto:

Experiment	Supporting Notebook Pages	Performed by
B	X-26645-100 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
C	X-26645-101 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
D	X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
E	X-26645-101 X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
F	X-26640-085 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owens
G	X-26640-087 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owen

Further evidence of the conception of one aspect of this invention is provided by page X-25982-100 from Mr. Owens notebook, also attached hereto.

4. Each of the dates deleted from the attached notebook pages is prior to August 5, 1999.

The undersigned declares further that all statements made herein on his own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with a knowledge that willful, false statements, and the like so made are punishable by fine, or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date

Linda Gail Bernard

Horst Clauberg

Michael John Cyr

John Walker Gilmer

James Christopher Matayabas, Jr.

Jeffery Todd Owens

Mark Edward Stewart

Sam Richard Turner

Date

Shriram Bagrodia



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Bernard et al.

Serial No.: 09/630,517

Group Art Unit: 1714

Filed: August 02, 2000

Examiner: K. I. Wyrozebski Lee

For: POLYAMIDE NANOCOMPOSITES WITH OXYGEN SCAVENGING
CAPABILITYCommissioner of Patents and Trademarks
Washington, D.C. 20231DECLARATION UNDER 37 CFR 1.131

We, Linda G. Bernard, Horst Clauberg, Michael J. Cyr, John W. Gilmer, James C. Matayabas, Jr., Jeffery T. Owens, Mark E. Stewart, Sam R. Turner, and Shriram Bagrodia declare that:

1. We are the coinventors of claims 1-29 of the above-identified patent application.
2. Prior to August 5, 1999, having earlier conceived the idea of recyclable polymer nanocomposite with improved oxygen and gas barrier properties comprising at least one polyamide resin, at least one oxygen-scavenging catalyst, and at least one layered silicate material, Linda G. Bernard, Jeffrey T. Owens, Marvin C. Hagey, and John W. Gilmer prepared the following polyamide polymer compositions, described herein, at the Research Laboratories of Eastman Chemical Co., Kingsport, Tennessee.
 - A) The following general procedures were used to measure oxygen consumption and carbon dioxide permeability. Oxygen consumption was measured on film samples, which were cut into strips, using a Columbus Instruments Micro-Oxymax respirometer with version 6.04b software. Samples were placed into a glass media bottle with a nominal volume of 250 mL. One empty bottle was included as a control blank. The bottles were attached to a ten port expansion module. Readings were taken at the start of the experiment and

MS 6/5/02

then every four hours. The instrument measured the change in the oxygen concentration from the previous reading in each cell and calculated the total oxygen consumption and rate based on the (previously measured) volume of the cell plus oxygen sensor system. The oxygen sensor is an electrochemical fuel cell. Carbon dioxide transmission rates were measured on film samples using a Mocon permeability analyzer.

- B) An unmodified MXD6 polyamide was prepared by extruding two trilayer films comprising internal layers of about 10 and 30 vol% of unmodified MXD6 6007, available from Mitsubishi Gas Company, with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were stretched using a T. M. Long instrument (4x4 orientation at about 110°C). The carbon dioxide transmission rates were 174 and 59 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively.

A MXD6 polyamide composition containing about 4000 ppm cobalt acetate as an oxygen-scavenging catalyst was prepared by mixing 250 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, and 4.23 grams of cobalt acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes then cooling. X-ray analysis of the product showed the concentration of cobalt in the product to be about 4000 ppm. This cobalt-containing polyamide (10 parts) was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company, at 250°C, to give material with a cobalt concentration about 400 ppm. The polyamide was used to prepare trilayer films and 2-inch square sections of the films were stretched as described above. The carbon dioxide transmission rates of the oriented films were determined to be 168 and 54 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner polyamide layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% polyamide, was determined to be about 370 microliters of oxygen over a period of 136 hours.

C) Using the procedure of example B, an MXD6 polyamide composition containing a layered silicate material and cobalt as an oxygen-scavenging catalyst was prepared by mixing 215.75 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, 34.25 grams of SCPX-1578, an organoclay available from Southern Clay Products, and 4.23 grams of cobalt(II) acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes followed by cooling. Ten parts of this product was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company at about 260°C to give material with a cobalt concentration of about 400 ppm and silicate concentration (ash) of about 1.0 wt%.

Two trilayer films were extruded comprising internal layers of about 10 and 30 vol% of the above compounded MXD6 6007 with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as described above. The carbon dioxide transmission rates for the oriented films were 117 and 41 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner nanocomposite layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% nanocomposite, was determined to be about 680 microliters of oxygen over a period of 136 hours.

D) Another MXD6 polyamide composition containing an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example B was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. A trilayer film was extruded comprising internal layers of about 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were prepared and oriented as above. The carbon dioxide transmissions rate of the oriented films were 411 cc(STP) CO₂/meter²/24hr, for the 50 vol% films. Oxygen consumption for 10

grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the PET-polyamide composite was determined to be about 60 microliters of oxygen over a period of 136 hours.

- E) Another MXD6 polyamide composition containing a layered silicate material and an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example C was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. Two trilayer films were extruded comprising internal layers of about 30 and 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as above. The carbon dioxide transmissions rates of the oriented films were determined to be 317 and 291 cc(STP) CO₂/meter²/24hr, for the 30 and 50 vol% films respectively. Oxygen consumption for 10 grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the nanocomposite was determined to be about 60 microliters of oxygen over a period of 136 hours.
- F) A polyamide composition was prepared in which the oxygen-scavenging catalyst, cobalt, was intercalated into the polymer matrix through the layered silicate material. A Wyoming-type montmorillonite clay was prepared in which 50% of the sodium cations were exchanged with cobalt and 50% with protons. Ash content of the clay was 87.15 wt %, cobalt content was 1.23 %, and X-ray basal spacing was 1.25 nm. The treated clay was dry mixed with 269 parts of a low molecular weight poly(m-xylylene adipamide), with IV of about 0.41 dL/g. The mixture was dried at 110°C overnight in a vacuum oven then extruded. The extruded material showed good oxygen consumption.
- G) Another polyamide composition was prepared identically to E except the montmorillonite clay used in the composition had 50 % of the sodium cations are exchanged with cobalt(II), 25% with octadecyltrimethylammonium cations,

page 651ov

and 25 % with protons. The clay had a cobalt content of 0.99 %, and X-ray basal spacing of 1.34 nm. The extruded material showed good oxygen consumption.

3. Evidence supporting the above examples above are provided by copies of research notebook pages as set forth in the table below and attached hereto:

Experiment	Supporting Notebook Pages	Performed by
B	X-26645-100 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
C	X-26645-101 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
D	X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
E	X-26645-101 X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
F	X-26640-085 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owens
G	X-26640-087 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owen

Further evidence of the conception of one aspect of this invention is provided by page X-25982-100 from Mr. Owens notebook, also attached hereto.

4. Each of the dates deleted from the attached notebook pages is prior to August 5, 1999.

The undersigned declares further that all statements made herein on his own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with a knowledge that willful, false statements, and the like so made are punishable by fine, or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date

Linda Gail Bernard

Date

Horst Clauberg

June 5, 2002

Date

Michael John Cyr

Date

John Walker Gilmer

Date

James Christopher Matayabas, Jr.

Date

Jeffery Todd Owens

Date

Mark Edward Stewart

Date

Sam Richard Turner

Docket: 71111

PATENT

Date

Shriram Bagrodia

msl gls/jz



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Bernard et al.

Serial No.: 09/630,517

Group Art Unit: 1714

Filed: August 02, 2000

Examiner: K. I. Wyrozebski Lee

For: POLYAMIDE NANOCOMPOSITES WITH OXYGEN SCAVENGING
CAPABILITYCommissioner of Patents and Trademarks
Washington, D.C. 20231DECLARATION UNDER 37 CFR 1.131

We, Linda G. Bernard, Horst Clauberg, Michael J. Cyr, John W. Gilmer, James C. Matayabas, Jr., Jeffery T. Owens, Mark E. Stewart, Sam R. Turner, and Shriram Bagrodia declare that:

1. We are the coinventors of claims 1-29 of the above-identified patent application.
2. Prior to August 5, 1999, having earlier conceived the idea of recyclable polymer nanocomposite with improved oxygen and gas barrier properties comprising at least one polyamide resin, at least one oxygen-scavenging catalyst, and at least one layered silicate material, Linda G. Bernard, Jeffrey T. Owens, Marvin C. Hagey, and John W. Gilmer prepared the following polyamide polymer compositions, described herein, at the Research Laboratories of Eastman Chemical Co., Kingsport, Tennessee.
 - A) The following general procedures were used to measure oxygen consumption and carbon dioxide permeability. Oxygen consumption was measured on film samples, which were cut into strips, using a Columbus Instruments Micro-Oxymax respirometer with version 6.04b software. Samples were placed into a glass media bottle with a nominal volume of 250 mL. One empty bottle was included as a control blank. The bottles were attached to a ten port expansion module. Readings were taken at the start of the experiment and

then every four hours. The instrument measured the change in the oxygen concentration from the previous reading in each cell and calculated the total oxygen consumption and rate based on the (previously measured) volume of the cell plus oxygen sensor system. The oxygen sensor is an electrochemical fuel cell. Carbon dioxide transmission rates were measured on film samples using a Mocon permeability analyzer.

- B) An unmodified MXD6 polyamide was prepared by extruding two trilayer films comprising internal layers of about 10 and 30 vol% of unmodified MXD6 6007, available from Mitsubishi Gas Company, with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were stretched using a T. M. Long instrument (4x4 orientation at about 110°C). The carbon dioxide transmission rates were 174 and 59 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively.

A MXD6 polyamide composition containing about 4000 ppm cobalt acetate as an oxygen-scavenging catalyst was prepared by mixing 250 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, and 4.23 grams of cobalt acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes then cooling. X-ray analysis of the product showed the concentration of cobalt in the product to be about 4000 ppm. This cobalt-containing polyamide (10 parts) was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company, at 250°C, to give material with a cobalt concentration about 400 ppm. The polyamide was used to prepare trilayer films and 2-inch square sections of the films were stretched as described above. The carbon dioxide transmission rates of the oriented films were determined to be 168 and 54 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner polyamide layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% polyamide, was determined to be about 370 microliters of oxygen over a period of 136 hours.

C) Using the procedure of example B, an MXD6 polyamide composition containing a layered silicate material and cobalt as an oxygen-scavenging catalyst was prepared by mixing 215.75 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, 34.25 grams of SCPX-1578, an organoclay available from Southern Clay Products, and 4.23 grams of cobalt(II) acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes followed by cooling. Ten parts of this product was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company at about 260°C to give material with a cobalt concentration of about 400 ppm and silicate concentration (ash) of about 1.0 wt%.

Two trilayer films were extruded comprising internal layers of about 10 and 30 vol% of the above compounded MXD6 6007 with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as described above. The carbon dioxide transmission rates for the oriented films were 117 and 41 cc(STP) CO₂/meter²/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner nanocomposite layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% nanocomposite, was determined to be about 680 microliters of oxygen over a period of 136 hours.

D) Another MXD6 polyamide composition containing an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example B was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. A trilayer film was extruded comprising internal layers of about 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were prepared and oriented as above. The carbon dioxide transmissions rate of the oriented films were 411 cc(STP) CO₂/meter²/24hr, for the 50 vol% films. Oxygen consumption for 10

grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the PET-polyamide composite was determined to be about 60 microliters of oxygen over a period of 136 hours.

- E) Another MXD6 polyamide composition containing a layered silicate material and an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example C was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. Two trilayer films were extruded comprising internal layers of about 30 and 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as above. The carbon dioxide transmissions rates of the oriented films were determined to be 317 and 291 cc(STP) CO₂/meter²/24hr, for the 30 and 50 vol% films respectively. Oxygen consumption for 10 grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the nanocomposite was determined to be about 60 microliters of oxygen over a period of 136 hours.
- F) A polyamide composition was prepared in which the oxygen-scavenging catalyst, cobalt, was intercalated into the polymer matrix through the layered silicate material. A Wyoming-type montmorillonite clay was prepared in which 50% of the sodium cations were exchanged with cobalt and 50% with protons. Ash content of the clay was 87.15 wt %, cobalt content was 1.23 %, and X-ray basal spacing was 1.25 nm. The treated clay was dry mixed with 269 parts of a low molecular weight poly(m-xylylene adipamide), with IV of about 0.41 dL/g. The mixture was dried at 110°C overnight in a vacuum oven then extruded. The extruded material showed good oxygen consumption.
- G) Another polyamide composition was prepared identically to E except the montmorillonite clay used in the composition had 50 % of the sodium cations are exchanged with cobalt(II), 25% with octadecyltrimethylammonium cations,

and 25 % with protons. The clay had a cobalt content of 0.99 %, and X-ray basal spacing of 1.34 nm. The extruded material showed good oxygen consumption.

3. Evidence supporting the above examples above are provided by copies of research notebook pages as set forth in the table below and attached hereto:

Experiment	Supporting Notebook Pages	Performed by
B	X-26645-100 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
C	X-26645-101 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
D	X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
E	X-26645-101 X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
F	X-26640-085 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owens
G	X-26640-087 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owen

Further evidence of the conception of one aspect of this invention is provided by page X-25982-100 from Mr. Owens notebook, also attached hereto.

4. Each of the dates deleted from the attached notebook pages is prior to August 5, 1999.

The undersigned declares further that all statements made herein on his own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with a knowledge that willful, false statements, and the like so made are punishable by fine, or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date

Linda Gail Bernard

Date

Horst Clauberg

Date

Michael John Cyr

Date

John Walker Gilmer

Date
James Christopher Matayabas, Jr.

Date

Jeffery Todd Owens

Date

Mark Edward Stewart

Date

Sam Richard Turner

Date

Shriram Bagrodia